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Further Characterization of Sorbents for Environmental Sampling--II

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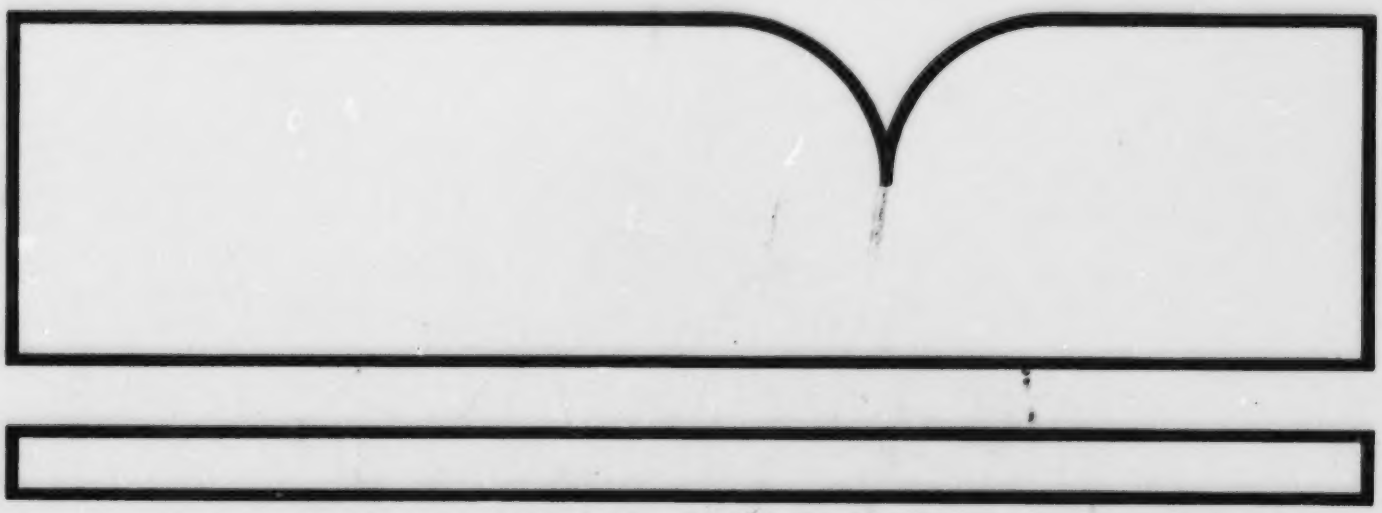

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FURTHER CHARACTERIZATION OF SORBENTS FOR ENVIRONMENTAL SAMPLING -- II

BY

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16. ABSTRACT The report is the fourth in a series providing characterization data related to the use of sorbents for emissions sampling. It provides retention and recovery data for several sorbates on XAD-2, XAD-7, Tenax-GC, Ambersorb XE-340, and Florisil. Retention properties of two organometallic compounds are given, and the effect of methane in a sample stream is shown. Mixed sorbent effects are shown to be negligible over all conditions studied.

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Sorbents	Stationary Sources	11G
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Organometallic Compounds		

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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	ii
LIST OF FIGURES	v
LIST OF TABLES	vi
ABSTRACT	vii
I. INTRODUCTION	1
II. BACKGROUND	2
III. APPROACH	5
A. Experimental Technique	5
B. Experimental Apparatus	6
C. Introduction of Sorbate Samples	9
D. Materials and Reagents	10
E. Recovery Studies	10
F. Effects of Methane Atmosphere on XAD-2	14
G. Effects on V_g of a Sorbate Mixture on XAD-2	15
H. Retention Volumes of Organometallics	15
I. Investigation of Additional Sorbents	15
J. Experimental Error	16
IV. RESULTS	22
A. Specific Retention Volume on Several Sorbents	22
1. Florisil	22
2. Amberlite XAD-7	22
3. Ambersorb XE-347	24
B. Recovery Studies	24
1. Hexane	24
2. Decane	26
3. Ethanol	27
4. Butanol	27
C. Retention Volumes of Organometallics	28
D. Effect of Methane Atmosphere on Retention of XAD-2	29
E. Effects of a Mixture of Sorbates on V_g using XAD-2	31
F. Thermal Stability of XE-348	31

TABLE OF CONTENTS (Continued)

		Page
V.	CONCLUSIONS	36
	A. Uncertainty in V_g Values	36
	B. Alternative Sorbents	36
	C. Organometallics	37
	D. Effects of Methane Atmospheres on V_g^T for XAD-2	37
	E. Effects of Mixtures of Sorbates	37
	REFERENCES	38

LIST OF FIGURES

Figure No.		Page
1	Relationship between Initial Retention Volume V_I and V_g^T	7
2	Gas Chromatographic Apparatus used to Determine V_g^T	8
3	Least Square Fit to All Data: Pentane on Florisil	19
4	Least Square Fit for One Experimental Series: Pentane on Florisil	20
5	Differential Scanning Calorimeter Traces for XE-340 Resin	34
6	Differential Scanning Calorimeter Traces for XE-348 Resin	35

LIST OF TABLES

Table No.		Page
1	Sorbates Used in the Study	11
2	Sorbents Used in the Study	11
3	Recovery Experiments	12
4	Specific Retention	17
5	Experimental V_g Data for Pentane on Florisil	18
6	Retention Volumes (V_g^{20}) on Several Sorbents	23
7	Recovery Studies Results	25
8	Effect of Methane on V_g^T	30
9	V_g of Mixed Sorbates on Resin	32

ABSTRACT

This work represents the continuation of a systematic study of the behavior of solid sorbents used to collect organic vapors from gaseous media. The studies were conducted using an elution analysis chromatographic method. The report deals with a series of experiments. Sorbents not used in earlier studies were examined to determine their specific retention volume and the percent recovery. Organometallics as a chemical class not previously used were studied to determine their retention volumes on some sorbents. The effect of methane on the recovery and the effect of mixed sorbents were also examined.

The resins used here included Tenax-GC, XAD-2, XAD-7, Ambersorb 340, Ambersorb 347, Ambersorb 348, and Florisil. One of them, Ambersorb 348, was found to be thermally unstable and was not recommended.

I. INTRODUCTION

This task involved a continuation of the systematic study of the use of solid sorbents to collect organic vapors from gaseous media. The use of an adsorbent-filled cartridge has become increasingly popular for sampling of organic vapors. The technique is used to sample source emissions and for ambient air concentrations. The use of these sorbents for environmental assessment studies has been adopted by the Process Measurement Branch of EPA by incorporating a sorbent trap in the SASS train. To support this application and gain a quantitative data base to guide in applications of the method, Arthur D. Little, Inc. has been carrying out research in this area for several years.

This report is the fourth in a series related to the use of sorbents for environmental sampling. The aims of this work were to:

- Investigate other resins to determine their applicability in terms of capacity, effectiveness and general usefulness;
- Investigate the recovery of several additional chemical classes from various resins;
- Investigate the effects of a mixture of sorbates on their retention on a resin;
- Determine the behavior of organometallics, particularly tetraethyllead and diethylmercury on various resins;
- Determine the effect of a mixed atmosphere containing methane on the retention of (specific) sorbates.

These studies were conducted using the elution analysis chromatographic method described previously.[1,2,3]

II. BACKGROUND

The previous work that was done at Arthur D. Little, Inc. has been reported in three parts. The first part[1] involved the investigation of two resins, XAD-2 and Tenax-GC, as collector resins in SASS train sorbent traps. From this preliminary work, various conclusions were drawn:

a. The retention volumes per gram of resin (V_g) for Tenax-GC and XAD-2 are about the same. Since XAD-2 has a bulk density about three times greater than Tenax-GC, it has a capacity three times greater than Tenax-GC per mL of resin. Assuming constant sorbent trap dimensions, a three times larger sample can be collected when using XAD-2.

b. Volumetric capacities of both resins show a regular dependence on the volatility of the compound used for testing.

c. XAD-2 resin in a SASS train sorbent trap operating for four hours will collect all materials boiling above 100-130°C, and Tenax-GC operating under the same conditions will collect all materials boiling over 120-150°C as long as they are not present in concentrations which will cause the weight capacity to be exceeded.

The second report[2] described further detailed studies based on the preliminary report recommendations.[1] The focus there was to support the use of chromatographic data to characterize these resins. A large number of sorbates were studied on XAD-2 and Tenax-GC. Specific retention volumes, V_g^T, were correlated with the physical properties of the adsorbate in order to determine V_g^T values reliably for other adsorbates. This study also determined that both resins, XAD-2 and Tenax-GC, show selectivity for nonpolar compounds. The effect of flow rate through the cartridge was investigated. Tenax-GC showed no

variance with flow rate while XAD-2 showed 15-20% lower V_g values for sorbates at very high flow rates (higher than would normally ever be encountered in a sampling train). This study also showed that the gas chromatographic elution volume technique used has distinct advantages for testing the resins because it requires small concentrations of sorbate and sorbent.

The third part of the study[3] focused on the effects of major combustion gas components, CO_2, H_2O, and combinations thereof on the adsorption behavior of XAD-2 and Tenax-GC. The study showed that XAD-2 is relatively unaffected by the combustion gas species while for Tenax-GC, the retention volume, V_g, was reduced by 22-43% in the presence of water vapor and an additional 25% when CO_2 was introduced. That work also began to investigate other sorbents to determine their intrinsic affinities, K_A. The affinities decreased in the order Charcoal Lot 104 > Ambersorb XE-340 > Charcoal Lot 106 > Ambersorb XE-347 > XAD-8 > Tenax-GC > XAD-2.[3]

The final phase of the work, which is reported here, investigated various specific topics which resulted from the previous studies. The key topics which were investigated were:

- A number of additional sorbents were studied to determine their intrinsic affinity for selected sorbates. The capacity of these sorbents (Florisil, XAD-7, XE-347) were investigated to determine their utility in sampling applications.
- Additional chemical classes, including organometallics, were studied on a number of resins.
- The recovery of three sorbates from six sorbents was determined.

- The possible competitive effects in sorbate mixtures were studied by examining the retention of two sorbates when present singly and in combination.
- The effect of methane gas, at a concentration that might be present in a fuel conversion or pyrolysis process effluent, on the retention behavior of sorbates was studied.

III. APPROACH

A. Experimental Technique

The method used in this study was that of chromatographic elution analysis.[2] In elution analysis, a small quantity of adsorbate is injected onto the sorbate cartridge in a very short time. The specific retention volume, V_g^T, can be determined for a sorbate on a particular sorbent from the resultant elution peak.

The specific retention volume, V_g^T, is the fundamental retention constant in gas chromatography and reflects the effect of flow rate, pressure drop, temperature, column void volume, and stationary phase weight (volume or surface area) on the retention of an injected solute. Knowledge of the value of V_g^T allows one to estimate the retention volume of a solute at another temperature or for a different sorbent cartridge size. Thus, V_g^T determined from short gas chromatographic columns packed with sorbent can aid in design of sorbent sampling modules.

Specific retention volumes, which actually correspond to the 50% breakthrough in an elution chromatography experiment, were computed in this study according to the following formula, which defines V_g^T at the temperature of the column oven in the chromatographic experiment. The derivation of this equation has been given elsewhere.[4]

$$V_g^T = \frac{jF_c(t_r - t_a)}{W_A}$$

Where V_g^T = specific retention volume for the adsorbate at column (sorbent trap) temperature;

F_c = flow rate of carrier gas at column temperature and pressure;

t_r = peak maximum retention time;

t_a = retention time for a completely nonsorbed solute;

W_A = adsorbent;

j = pressure correction.

The correspondence between V_g^T and the 50% breakthrough in an elution chromatography experiment is illustrated in Figure 1. The actual breakthrough of the sorbate begins to occur after V_I volumes of gas have passed over the sorbent bed. However, V_I is not routinely determined because its value is flow-rate dependent, shows a dependence on the packing structure of the sorbent column, and is difficult to precisely locate on the chromatogram. The specific retention volume, V_g^T, on the other hand, is easily located and is the only point on the chromatographic band corresponding to thermodynamic equilibrium. A safety factor can be built into any calculation of breakthrough volume to account for the disparity between V_g^T and V_I.

The specific retention volume, V_g^T, for a sorbate on a sorbent is directly related to the equilibrium adsorption coefficient, K_A, so long as the experiments are carried out at low sorbate concentrations (the Henry's Law region). Under these conditions:

$$V_g^T = K_A^* A_s^\circ$$

where V_g^T = specific retention volume;

K_A^* = equilibrium adsorption coefficient;

A_s° = adsorbent specific surface area.

B. Experimental Apparatus

Figure 2 is a schematic of the basic apparatus used to determine elution volumes, V_g^T, in this study and is described in the previous studies.[2] Principal components of the apparatus are: the sorbent cartridge, the gas chromatograph, and the pressure, flow and temperature measuring systems.

The sorbent cartridges were proportionally scaled down from the typical cross-section of a SASS train sorbent resin canister. Stainless steel tubing 9 cm long, 0.45 to 0.51 cm I.D., and 0.64 cm O.D. was used to

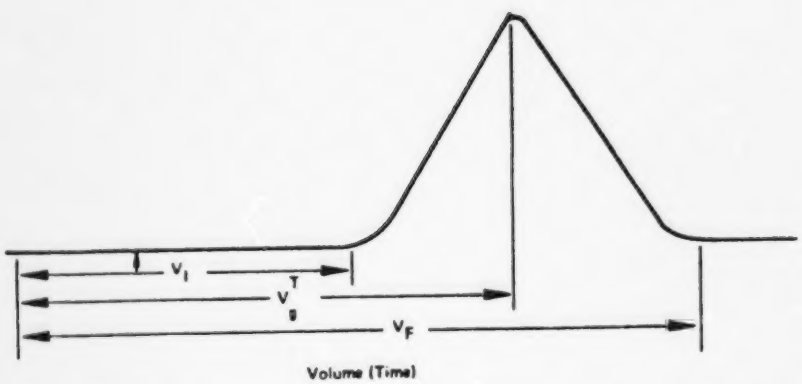

FIGURE 1

RELATIONSHIP BETWEEN INITIAL RETENTION VOLUME V_I AND V_g^T

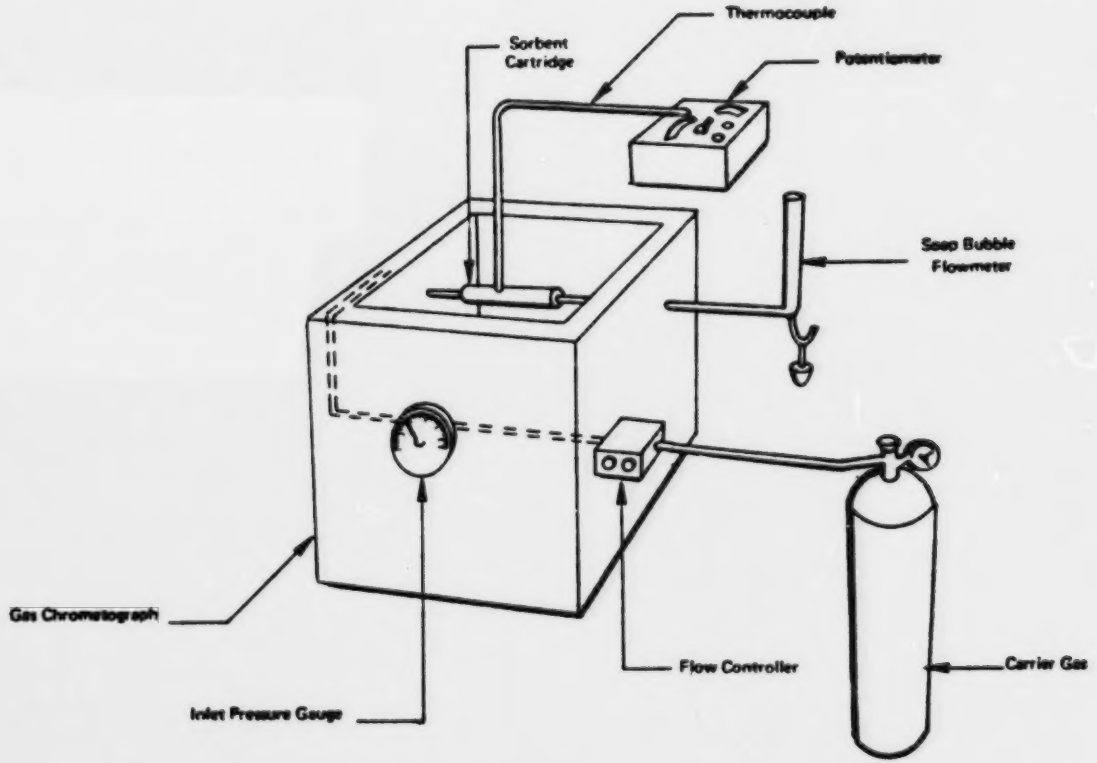

FIGURE 2

GAS CHROMATOGRAPHIC APPARATUS USED TO DETERMINE V_g^T

contain the resin. The sorbent cartridge was connected to two 0.64 cm x 0.16 cm (1/4 in x 1/16 in) reducing unions drilled out to minimize dead volume. The resin was retained in the trap by stainless steel frits at the end of the tubing. Connections to the chromatograph were made with 0.16 cm tubing.

The two gas chromatographs employed in this study were a Varian Model 1200, a single column instrument employing a flame ionization detector, and a Gow-Mac 550 dual column instrument employing a thermal conductivity detector. The thermal conductivity detector was used in the methane atmosphere study in order to overcome the effects of the high concentration of methane on sorbate detection.

The column head pressure on the gas chromatographs was read with a U-tube mercury-filled manometer; the pressure reading was taken by puncturing the injection septum with a No. 23 gauge conical point Hamilton needle with side hole, connected via Tygon tubing to the manometer. On the Varian 1200, flow control was provided by a Brooks Model 8743 flow controller. The retention volume data were collected at maximum electrometer sensitivity and recorded on a Hewlett-Packard Model 7133A recorder.

The column temperatures were measured with the aid of a Rubicon potentiometer. Iron-constant thermocouples (No. 20) were placed in contact with the sorbent cartridge and connected to the potentiometer. To offset the effect of a "line" room temperature EMF generating junction, a second thermocouple was connected in series with the oven thermocouple, and was immersed in an ice bath. The injector and detector temperature were kept at 250°C. Total gas flow rates were measured using a soap bubble flow meter.

C. Introduction of Sorbate Samples

The sample introduction technique used in the elution analysis studies consisted of taking up a small amount (<0.5 μL) of liquid sorbate in a 10 μL syringe, then expelling the liquid, and pumping the syringe 50 or

more times. This allowed generation of a reproducible dilute sorbate vapor concentration. With the resulting low concentration samples (<10 ppm), the experiments could be conducted in the Henry's Law region.

Three to five replicate elution experiments were run for each set of chromatographic conditions.

D. Materials and Reagents

The helium used was prepared by Linde, a division of Union Carbide, and obtained through Welders Supply of Billerica, Massachusetts.

The methane-in-helium used in the study of the effects of other gases was 1.1% methane, certified standard, obtained from Matheson Gas Products.

The sorbates and sorbents used, and source of supply, are given in Tables 1 and 2.

The Tenax-GC was used as received. The resins obtained from Rohm and Haas were cleaned by several rinses with water, then extracted with methanol for 24 hours followed by methylene chloride extraction for the same period. They were then dried under a stream of nitrogen. The Florisil was Soxhlet extracted with hexane for eight hours, dried at 110°C for eight hours, activated at 650°C in a muffle furnace, cooled to 110°C, and stored at that temperature until use.

E. Recovery Studies

The suitability for sorbents for their intended purpose of sampling organic vapors from air depends on the recovery of sorbates from the resins as well as on the collection efficiency measured by V_g. Recovery experiments were conducted using four sorbates--hexane, decane, ethanol, and n-butanol--on six solid sorbents--XAD-2, Tenax-GC, charcoal, Florisil, XE-340, and XAD-7. Table 3 indicates the sorbate:sorbent combinations that were studied.

TABLE 1

SORBATES USED IN THE STUDY

Sorbate	Source
Pentane	Burdick and Jackson
Hexane	Burdick and Jackson
Decane	Poly Science Corporation
1,2-Dichloroethane	Fisher
1,2-Dichloropropane	Fisher
Chlorobenzene	Fisher
1,4-Dichlorobenzene	Fisher
Ethanol	Gold Shield
n-Propanol	Poly Science Corporation
n-Butanol	Poly Science Corporation

TABLE 2

SORBENTS USED IN THE STUDY

Sorbent	Source
Tenax-GC	Applied Science Laboratories
XAD-2	Rohm and Haas
XAD-7	Rohm and Haas
Ambersorb 340	Rohm and Haas
Ambersorb 347	Rohm and Haas
Ambersorb 348	Rohm and Haas
Florisil	Applied Science Laboratories

TABLE 3

RECOVERY EXPERIMENTS

	XAD-2	XAD-7	Tenax-GC	Petroleum Base Charcoal (Lot 104)	XE-340	Florisil
Hexane	x	x	x	x	x	x
Decane	x	x	x	-	x	x
n-Butanol	-	x	-	x	x	-
Ethanol	-	-	-	x	x	-

- Experiment not done.

The percent recovery of the sorbate from the sorbent was determined by challenging the sorbent with a known concentration of sorbate in air for a given amount of time. The sorbents were desorbed in appropriate solvents and the resulting solutions were analyzed to determine the quantity of sorbate recovered from the resin. The quantity of the sorbate recovered from the resin was compared to the quantity that was collected (concentration in mg/m^3 x sampling rate in m^3/min x sampling time in min). A collection efficiency of 100% was assumed; the sample volume in each case was substantially less than the volumetric breakthrough capacity calculated from V_g data for that particular sorbate:sorbent system. The amount of each sorbent used was as follows:

Lot 104 Charcoal	- 100 mg
XAD-2	- 100 mg
Tenax-GC	- 400 mg
XAD-7	- 100 mg
XE-340	- 100 mg
Florisil	- 400 mg

Each test atmosphere was generated by means of continuous direct injection of liquid sorbate into a "vapor dilution/sampling system" developed under other programs.[5] The method for generating the vapor and the dilution sampling system are described briefly here.

The vapor generation/dilution system basically consists of a main line air stream to which are added predetermined amounts of various liquids to generate the desired vapor at known concentrations. From the main line, three branch off; six sampling devices are connected to two of the lines, and twelve sampling devices are connected to the third line. All these sampling devices are connected in parallel via critical flow orifices (CFOs) to a vacuum line. Air flow rates through the system are established by means of critical flow orifices and flow restrictors. The primary air system derived from compressed air is maintained at 20.0 psig. The appropriate flow restrictors are chosen to maintain an air flow of approximately 0.1 m^3/min in the main line.

Vapor concentrations from liquids are generated by adding known amounts of liquid to the main line of the vapor dilution/sampling apparatus. A continuous delivery rate is achieved using a Harvard Model 944 Syringe Drive. The syringe is connected to a 25-gauge stainless steel needle in the main line by a short length of 0.16 cm (1/16 in) O.D. Teflon tubing.

The approximate delivery rates of the syringe drive are known at each setting for several syringe sizes based upon preliminary calibrations. The syringe is then filled and connected to a weighing bottle, and the drive is activated for a period of time to allow the actual delivery rate, in mg/min, to be determined by weighing the amount collected. Sufficient time is allowed to provide a weight change which can be measured reliably and, thus, enable a precise calibration. Usually, 25-800 mg are collected depending on the specific compound being studied.

F. Effects of Methane Atmosphere on XAD-2

In the previous work,[3] studies were done to determine the effect of major components of stack gas--carbon dioxide and water vapor--on the resin. For some sources, methane is found also in stack gases at appreciable concentrations (thousands of parts per million). Its effect on V_g is reported here. Retention volumes were determined for four sorbates--n-pentanol, n-butanol, n-octane, and n-hexane--on XAD-2 at different column temperatures and two different atmospheres, with or without 1.1% methane in helium. The sorbates were selected to represent the classes of compounds, aliphatic hydrocarbons and alcohols, which had major differences in elution behavior. The Kiselev classification[6] for the aliphatic hydrocarbons is Group A (nonpolar) and for the alcohols is Group D (highly polar). Specific compounds were chosen to have a reliably measured retention time (three to ten minutes) at a given temperature.

The V_g value for each sorbate was determined at three temperatures with 1.1% (vol/vol) methane in helium carrier gas and with pure helium carrier gas.

G. Effects on V_g of a Sorbate Mixture on XAD-2

In addition to evaluating the effect of gases such as carbon dioxide and methane on the sorbate, it is useful to determine the possible competitive effects in a mixture of sorbates whose elution behavior is considerably different from each other. The sorbates used in this experiment and their Kiselev classification were: n-heptane - Group A; ethylbenzene - Group B; n-butanol - Group D.[6]

The mixture of sorbates used for the experiment was made up in a 3 mL crimp top vial. Several microliters (10 to 15) were added to the vial, which was then sealed. The mixture was allowed to equilibrate for an hour before injections of the head space gases were made. The experiments were carried out on a Varian 1200, employing flame ionization detection. The method of elution chromatography was used.

The three-component mixture was analyzed four times at 137.8°C. The individual components of the mixture were also analyzed three to six times each under the same conditions as the mixture.

H. Retention Volumes of Organometallics

Only one of the Kiselev classes,[6] organometallics, Group C, had not been investigated in previous work. Tetraethyllead and diethylmercury, which are both stable in air, were used to investigate this group. The retention volumes for these two compounds were determined on XAD-2.

Dilute vapors (10 ppm) of the organometallics were made up in 2-liter glass bulbs. Blank samples from the glass bulbs were analyzed to ensure they were clean. Ten microliters of the organometallic were injected into the bulb and allowed to equilibrate. One milliliter of the resultant gas mixture was injected into the chromatograph.

I. Investigation of Additional Sorbents

In previous work, it had been shown that XAD-2, among other sorbents, had good retention characteristics for a wide range of nonpolar organics.

However, a satisfactory collection medium for highly volatile and polar species such as low molecular weight alcohols had not been identified. Table 4 shows the additional sorbents that were investigated in this work as candidates for collection of volatile and polar species.

J. Experimental Error

Some of the values calculated for V_g^{20} for various experimental conditions appear to vary in ways not easily attributable to experimental variables. Various sources of error which exist in the measurement and in the experimental conditions will propagate through the calculations to the final value for V_g^{20}.

In earlier work, the precision of the V_g measurements was determined by replicate injections onto a sorbent cartridge. The reproducibility was on the order of $\pm$ 3%. In this work, when repeating some early data, variations in V_g larger than expected from earlier work were discovered. Therefore, in order to obtain an estimate of the magnitude of the error that can exist in the determination of V_g^{20}, the values of V_g were recalculated using all the available data. The following discussion indicates the magnitude of errors that may be encountered.

Table 5 lists all the available experimental data from this and previous work[3] for pentane on Florisil. Figure 3 shows a plot of log V vs 1/T(°K) for these data. The error bars shown illustrate the variance observed for replicate measurements within a particular set of analyses. The line is the linear least square fit to the seven points. The correlation coefficient, which is a measure of the fit of the line to the data, was 0.53. This indicates that the fit to this line was very poor. Figure 4 is a similar plot of log V_g vs 1/T for pentane on Florisil where the same cartridge had been used for all measurements. The correlation coefficient for this linear fit was much better at 0.98.

The same situation is observed in the case of hexane on Florisil. Using all available data points, the correlation coefficient was 0.56. Looking

TABLE 4

SPECIFIC RETENTION

	Florisil	XAD-7	XE-347
Pentane	x	x	
Hexane	x	x	
Octane			
Ethanol		x	x
1,2-Dichloroethane	x		
1,2-Dichloropropane	x		
Chlorobenzene	x		
1,4-Dichlorobenzene	x		
n-Propanol	x		
n-Butanol	x	x	x
n-Pentanol			

x = Retention experiments He atmosphere

TABLE 5

EXPERIMENTAL V_g DATA FOR PENTANE ON FLORISIL

Colum. Temp.	V_g	$\overline{V_g}$	$V_{g\,max.}$	$V_{g\,min.}$	Amount of Resin
121.5	21.5 21.5 21.5 21.5 21.5	21.5	21.5	21.5	1.16
133	22.2 24.4 22.2 22.2	22.8	24.4	22.2	1.17
121.3	26.4 26.4 27.7 25.0	26.4	27.7	25.0	1.17
102	46.0 43.9 41.8 43.9 43.9	43.9	46.0	41.8	1.17
122.0	49.2 50.9 49.2 50.9 49.9	50.0	49.2	50.9	1.23
140.7	35.5 37.3 36.4 35.5 36.4	36.2	37.3	35.5	1.23
107.6	92.7 86.1 96.1 86.1 86.1	89.4	96.1	86.1	1.23

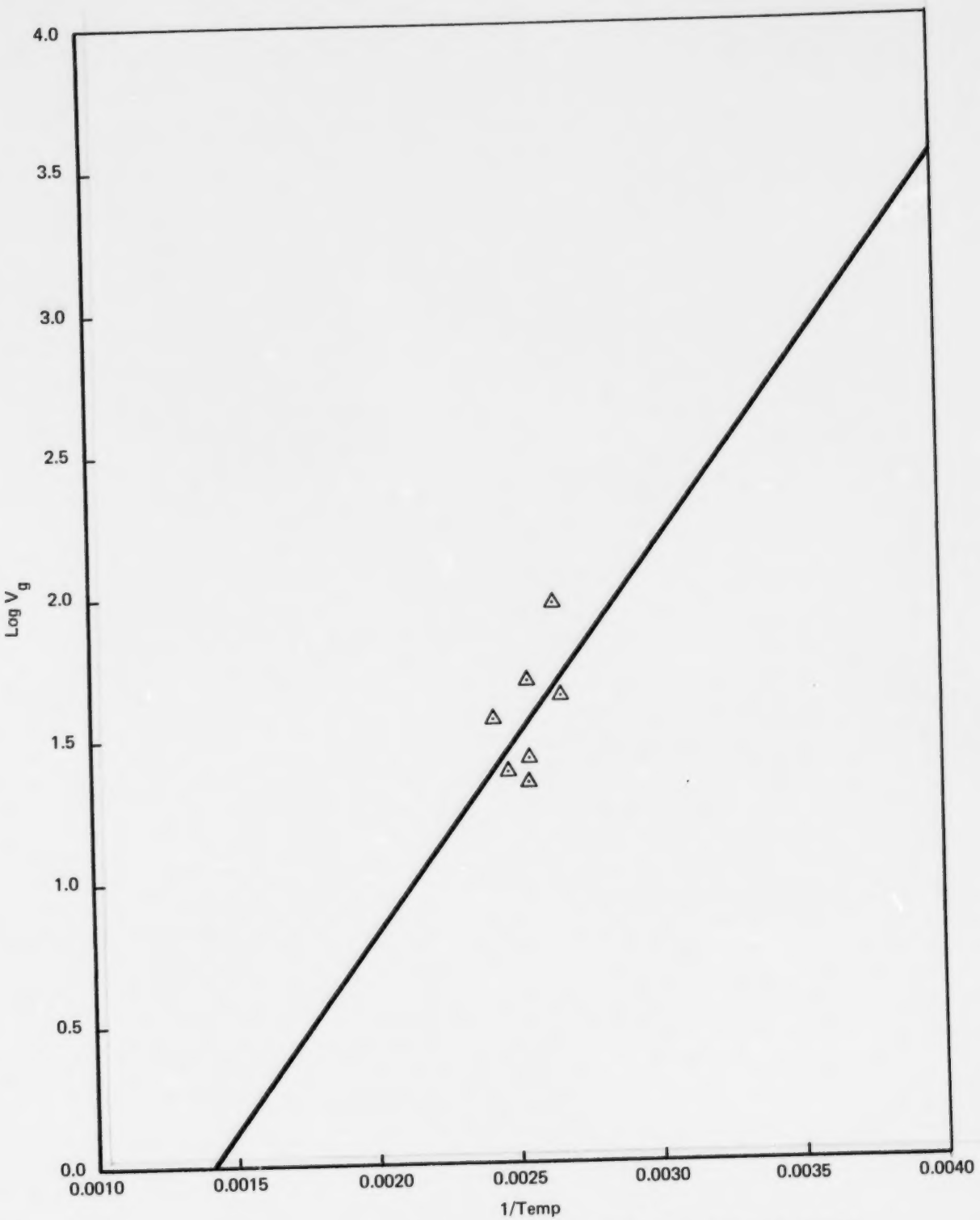

FIGURE 3 LEAST SQUARE FIT TO ALL DATA: PENTANE ON FLORISIL

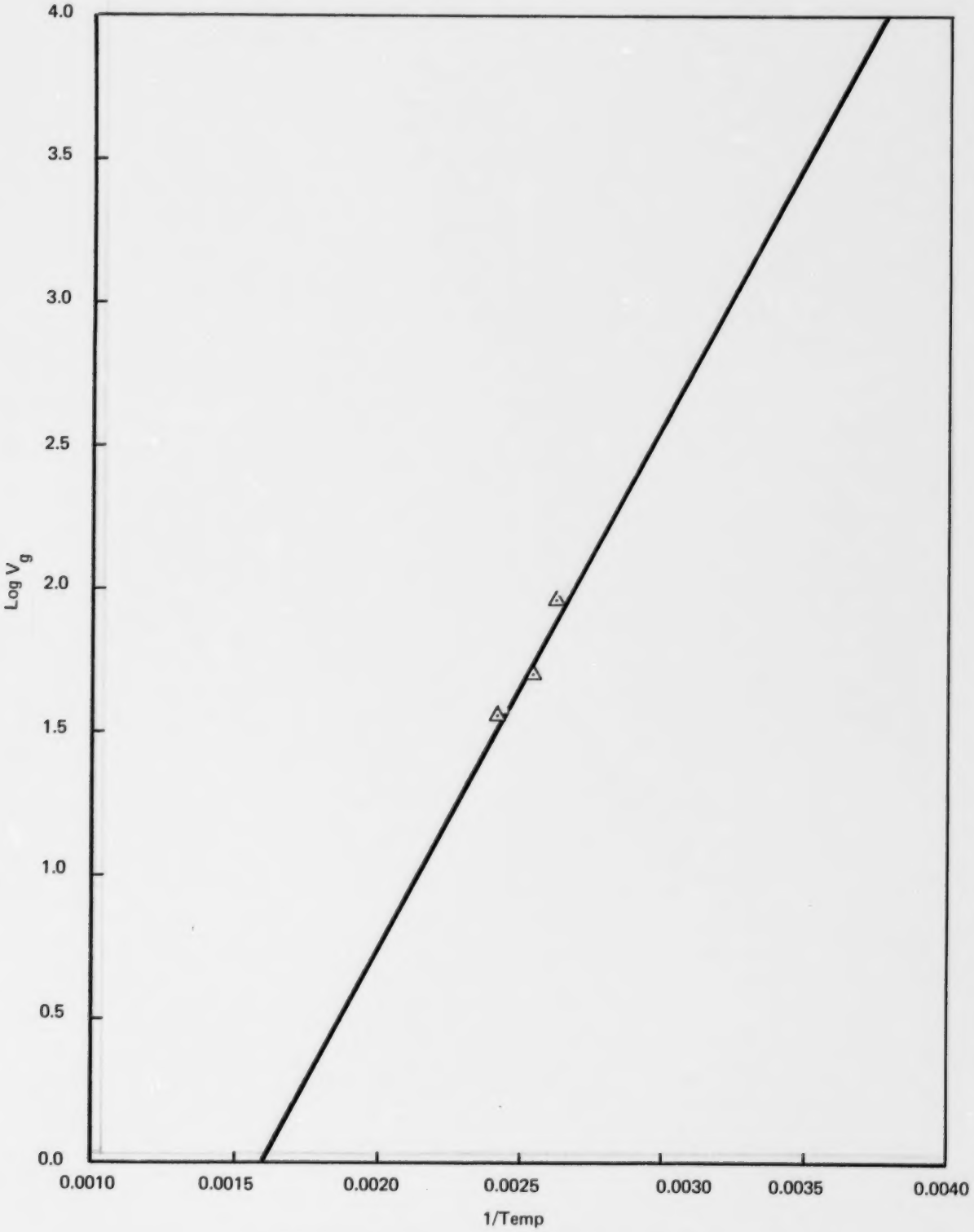

FIGURE 4 **LEAST SQUARE FIT FOR ONE EXPERIMENTAL SERIES: PENTANE ON FLORISIL**

at a case where the same sorbent cartridge was used, the correlation coefficient rose to 0.98 for one cartridge, 1.00 for the other. These least square fits correspond to V_g^{20} of 3.5×10^3 for all data points, 1.5×10^4 for the single cartridge. Since the precision within a given run is good, it appears that variability between sorbent cartridges is the cause of the large overall deviation. Channeling due to irreducible cartridge packing is one possible source of variability.

The variability observed in these replicate determinations of V_g for n-alkanes on Florisil sorbent suggests that extrapolated values of V_g^{20} may be uncertain by as much as a factor of 4 or 5. This uncertainty should be taken into account when comparing data for different sorbates on one sorbent or one sorbate on several sorbents, and in designing sorbent sampling systems with appropriate margins of safety to assure quantitative collection of a given sorbate.

IV. RESULTS

A. Specific Retention Volume on Several Sorbents

Table 6 presents a summary of the retention volume data that were generated in this study of additional sorbents. The V_g^{20} values obtained for the same sorbates on Tenax-GC and XAD-2 are included for reference.

1. Florisil

Florisil has been recommended[7] as a collection medium for PCBs from air. For this reason, the chlorinated compounds were chosen as test compounds for this sorbent. Both aromatic and aliphatic chlorinated compounds were run for comparison.

Florisil is a magnesium silicate which has high thermal stability. This allows it to be activated at high temperature prior to use, thus removing most traces of organics and yielding very low organic blank or background levels.

The vapor retention behavior of Florisil is similar to that of polymeric resins for aliphatics, alcohols and chlorinated aromatics. It would not be expected that Florisil has any great advantage over the resin sorbents for sampling PCBs in terms of volumetric capacity. On the other hand, greater affinity is shown for the chlorinated aliphatics on Florisil than on any of the other sorbates tested (Table 6).

Florisil seems to exhibit an incrementally greater affinity for the halogen character of a molecule than for the molecule's polarity or aromaticity.

2. Amberlite XAD-7

Amberlite XAD-7 is a polymeric acrylic ester resin whose behavior for aliphatic compounds is similar to those of XAD-2 and Tenax-GC. The more polar XAD-7 resin exhibits a greater affinity for alcohols (two-to-three orders of magnitude greater V_g's) than do XAD-2 and Tenax-GC (Table 6).

TABLE 6

RETENTION VOLUMES (V_g^{20}) ON SEVERAL SORBENTS

Sorbent / Sorbate	Florisil	XAD-7	XE-347	XAD-2	Tenax-GC
Pentane	8×10^2	1×10^4	---	2×10^4	2×10^3
Hexane	2×10^4	1×10^5	---	7×10^4	3×10^4
n-Propanol	1×10^4	9×10^6	---	7×10^3	7×10^3
n-Butanol	2×10^3	---	2×10^6	2×10^4*	4×10^4
1,2-Dichloroethane	8×10^8	---	---	2×10^4+	2×10^4
1,2-Dichloropropane	8×10^8	---	---	---	1×10^5
Chlorobenzene	2×10^6	---	---	2×10^6+	2×10^6
1,4-Dichlorobenzene	2×10^6	---	---	2×10^6	2×10^7
Ethanol	---	2×10^5	4×10^6	2×10^3*	9×10^2*

*From Reference 3

+From Reference 2

3. Ambersorb XE-347

Ambersorb XE-347, a carbonacous adsorbent, has a chemical behavior which is intermediate between activated charcoal and the polymeric resins. It is a relatively new resin. The retention volume for the alcohols studied on this sorbent are listed in Table 6.

B. Recovery Studies

In the recovery studies, four sorbates were studied on six different sorbents and the results are described below.

1. Hexane

An atmosphere of 35.9 mg/m^3 was generated using the vapor generator. Twenty-four samples, four for each resin, were collected at 0.05 L/min for 60 minutes, resulting in the adsorption of 0.108 mg.

Hexane samples were desorbed in solvent containing internal standard as follows:

Sorbent	Internal Standard	Volume
Charcoal	$C_{10}H_{24}$ in CH_2Cl_2	1.0 mL
XAD-2	$C_{10}H_{24}$ in CH_2Cl_2	1.0 mL
Tenax-GC	$C_{10}H_{24}$ in ethylacetate*	5.0 mL
XAD-7	$C_{10}H_{24}$ in CH_2Cl_2	1.0 mL
XE-340	$C_{10}H_{24}$ in CH_2Cl_2	1.0 mL
Florisil	$C_{10}H_{24}$ in CH_2Cl_2	2.0 mL

*Ethylacetate was used because Tenax-GC is incompatible with methylene chloride.

The mean recoveries and coefficients (CV) of variation for hexane and the other sorbates are shown in Table 7.

The recovery of hexane is 100 $\pm$ 10% for four of the six sorbents tested. The slightly higher apparent recovery value for XAD-7 may reflect a

TABLE 7

RECOVERY STUDIES RESULTS

Sorbate / Sorbent	Hexane		Decane		Ethanol		Butanol	
	% Recovery	CV	% Recovery	CV	% Recovery	CV	% Recovery	CV
Charcoal	97	21.0%	--*	--	47.2	6.3	81.3	3.9
XAD-2	92	8.6%	88.2	6.4	--*		--*	
Tenax-GC	102	9.8%	97.4	4.0	--*		--*	
XAD-7	114	8.9%	96.5	15.5	--*		46.3	9.1
XE-340	109	5.9%	88.0	5.4	75.3	3.3	88.2	8.9
Florisil	25	17.0%	80.1	6.0	--*		--*	

*Not determined; see text for explanation.

chromatographic interference in the analysis. However, this deviation is only slightly higher than the average coefficient of variation for the experiments, which is about 12%. A major source of the variation is probably the calibration of the generating system.

The very low recovery for hexane-Florisil was not expected. It is interesting to note that there was good recovery of decane on this sorbent.

2. Decane

An atmosphere containing 58.11 mg/m^3 of decane in air was generated using the vapor generator. Four replicate samples for each of the five resins were collected at 0.05 L/min for 60 minutes, resulting in the adsorption of 0.174 mg.

The samples were desorbed in solvent containing internal standard (hexane) as follows:

Sorbent	Internal Standard	Volume
XAD-2	C_6H_{14} in CH_2Cl_2	1.0 mL
Tenax-GC	C_6H_{14} in ethylacetate*	1.0 mL
XAD-7	C_6H_{14} in CH_2Cl_2	5.0 mL
XE-340	C_6H_{14} in CH_2Cl_2	1.0 mL
Florisil	C_6H_{14} in CH_2Cl_2	2.0 mL

*Ethylacetate was used because Tenax-GC is incompatible with methylene chloride.

The recovery data for decane are shown in Table 7. An adequate set of recovery data for decane on charcoal was not acquired because of sample breakage.

The desorption efficiencies obtained on charcoal from the NIOSH studies[5] should be a good approximation for this study and they are summarized on the following page.

Sorbate	Concentration ppm	Concentration mg/m^3	% Recovery (Desorption Efficiency)
Heptane	250	1000	95.9
Octane	250	1275	92.9

The desorbing solvent used with the two alkanes above was carbon disulfide.

3. Ethanol

An ethanol atmosphere of 20.15 mg/m^3 in air was generated and eight samples were collected at 0.05 L/min for 100 minutes, resulting in the adsorption of 0.101 mg. Four samples were collected on each of the two resins that were suitable candidates for ethanol sampling, based on V_g values. Tenax-GC, XAD-2 and Florisil were not tested due to their low volumetric capacity for ethanol. XAD-7 could not be evaluated due to the lack of a compatible desorbing solvent which would allow adequate chromatographic separation. The V_g^{20} values for charcoal, 3×10^6 mL/g, and XE-340, 2×10^5 mL/g, were large enough to allow the recovery studies to be conducted.

The samples were desorbed in solvent containing internal standard (n-butanol) as follows:

Sorbent	Internal Standard	Volume
Charcoal	C_4H_9OH in CS_2	1.0 mL
XE-340	C_4H_9OH in CS_2	1.0 mL

The change in desorbing solvent from methylene chloride to carbon disulfide was necessary to allow resolution of the ethanol from the solvent front in the GC analysis. The mean recoveries and coefficients of variation (CV) are listed in Table 7.

4. Butanol

In the n-butanol study, an atmosphere of 30.65 mg/m^3 was generated using the vapor generator, resulting in the adsorption of 0.153 mg. Four

samples for each of the three resins were collected at 0.06 L/min for 100 minutes.

The samples were desorbed in solvent containing internal standard (ethanol) as follows:

Sorbent	Internal Standard	Volume
Charcoal	C_2H_5OH in CS_2	1.0 mL
XAD-7	C_2H_5OH in CH_2Cl_2	1.0 mL
XE-340	C_2H_5OH in CS_2	1.0 mL

The mean recoveries and coefficients of variation are shown in Table 7.

XAD-2, Tenax-GC and Florisil could not be tested accurately due to their low volumetric capacity.

C. Retention Volumes of Organometallics

The organometallic category is the only Kiselev category which had not been examined on the sorbates. In air sampling, it is possible that some members of this category would be present and knowledge of their retention behavior would be useful.

Retention volumes for tetraethyllead and diethylmercury on XAD-2 have been determined. These two particular organometallics were investigated because they are sufficiently volatile to be tested, and they are stable in air.

As in previous work,[2,3] values of V_g^{20} for these sorbates were calculated by extrapolation of chromatographic retention data obtained at elevated temperatures. The resulting data were:

Sorbate	Boiling Point °C	V_g^{20} (mL/g)
Tetraethyllead	200	5×10^{10}
Diethylmercury	159	6×10^{5}

The V_g^{20} for tetraethyllead (TEL) is the largest observed on XAD-2, and is considerably higher than would have been predicted on the basis of V_g data for organic species with similar boiling points. For example, the V_g^{20} value previously obtained[2] for p-cresol (b.p. 202°C) was 1.5×10^7, 3000 times lower than the apparent V_g^{20} for TEL. On the other hand, the measured values of V_g^T at the experimental temperature were quite similar for p-cresol (439 mL/g at 185°C) and for TEL (309 mL/g at 189°C). This implies that the large V_g^{20} for TEL arises from a more dramatic temperature dependence of V_g compared to the organic species previously studied.

The apparent slope of the log V_g vs 1/T curve for TEL implies a large enthalpy of adsorption. The heat of adsorption, ΔH_A, provides a measure of the interaction between resin matrix and the sorbent molecule. The ΔH_A values for the two compounds are:

Tetraethyllead	-30 kcal/mole
Diethylmercury	-14 kcal/mole

The ΔH_A for the organolead compound is extremely high compared to ΔH_A from earlier work[2] which ranged from -10 to -18 kcal/mole. Although it is possible that there is a highly specific strong interaction between TEL and XAD-2, it is not clear what the nature of that interaction might be. It seems more probable that the calculated ΔH and slope values are in error. Unfortunately, it is not possible to measure V_g at temperatures much lower or much higher than those used here. It was, therefore, not practical to obtain a better measurement of the temperature dependence of the TEL V_g value in this program.

D. Effect of Methane Atmosphere on Retention of XAD-2

The effect of methane on retention of organic sorbates was investigated using a 1.1% (11,000 ppm) mixture of methane in helium as a carrier gas. The data is given in Table 8. At corresponding experimental temperatures, the V_g's are very similar. This indicates that the presence of methane at thousands of parts per million concentration in

TABLE 8

EFFECT OF METHANE ON V_g^T

Condition / Sorbate	Column Temperature (°C)	% Methane Atmosphere	Vg (mL/g)
n-BUTANOL	120.2	0.0	182
	121.6	1.1	178
	130.9	0.0	125
	130.9	1.1	132
	132.7	0.0	116
	132.7	1.1	120
n-PENTANOL	115.5	0.0	558
	116.2	1.1	580
	137.8	0.0	268
	137.8	1.1	266
	147.4	0.0	181
	147.0	1.1	178
n-HEXANE	115.5	0.0	202
	116.2	1.1	221
	137.8	0.0	121
	137.8	1.1	129
	147.4	0.0	82
	147.0	1.1	82
n-OCTANE	120.2	0.0	1130
	121.6	1.1	1160
	132.7	0.0	632
	132.7	1.1	620
	144.4	0.0	461
	141.8	1.1	448

the sampled stream would not be expected to reduce the efficiency of the sorbent.

E. Effects of a Mixture of Sorbates on V_g Using XAD-2

Previous experimental determinations of V_g have been done using only one sorbate. This is an idealized situation and effects of mixed sorbates on XAD-2 were studied. The Kiselev classification of the sorbates used were: n-heptane - Group A; ethylbenzene - Group B; and n-butanol - Group D.

Three component mixtures were analyzed at 137.8°C. The individual components were also analyzed three to six times each under conditions identical to that of the mixture. Table 9 lists the data for these experiments. The V_g values are means obtained from a series of runs.

In comparing the V_g of each sorbate in the mixture with the V_g of the pure sorbate, the difference in retention volumes was negligible. Any differences seen (2-5%) are within the range of experimental error.

F. Thermal Stability of XE-348

In the experiments to determine the V_g's on Ambersorb XE-348, it was observed that the retention volume appeared to be increasing when the temperature of the experiment (253°C to 319°C) was increased. Normal behavior of the sorbent systems is the opposite; sorbates typically break through faster at higher temperatures. In an attempt to determine the cause of this behavior, a Differential Scanning Calorimeter (DSC) analysis was run to detect phase transitions which might occur as well as look for evidence of decomposition. Previously, all the polymeric resins had undergone Thermal Gravimetric Analysis (TGA) to determine their upper temperature stability limits.[1,2,3] The TGA had indicated that XE-348 should not decompose up to 320°C, but had not ruled out the possibility of a phase change.

TABLE 9

V_g OF MIXED SORBATES ON RESIN*

Sorbate	V_g (mL/g) (Mixture)	V_g (mL/g) (Alone)	$\left(\frac{V_g \text{ mixture}}{V_g \text{ alone}}\right)$
n-Heptane	263	242	0.98
Ethylbenzene	620	637	0.97
n-Butanol	118	112	1.05

*All data at 137.8°C

Figure 5 is a DSC of XE-340 provided for reference. The trace labeled "y" is the readout from the instrument. The trace labeled "dy" is the derivative of "y." Figure 6 is the DSC for XE-348. As can be seen from the DSC for XE-348, there is an endothermic transition between 75°C and 200°C. This change in the physical state of the XE-348 may be the reason why the retention behavior behaves anomously on this resin. No similar changes were observed in the XE-340 resin.

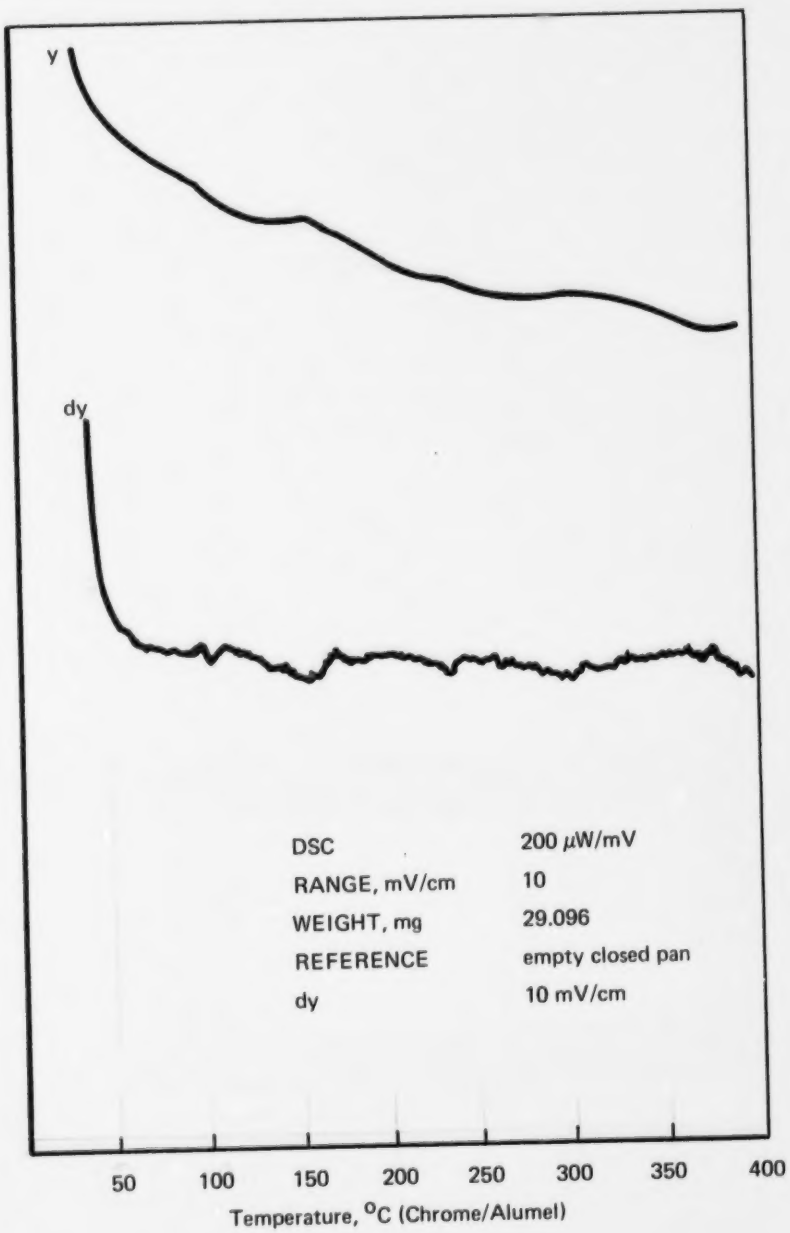

FIGURE 5 DIFFERENTIAL SCANNING CALORIMETER TRACES FOR XE-340 RESIN

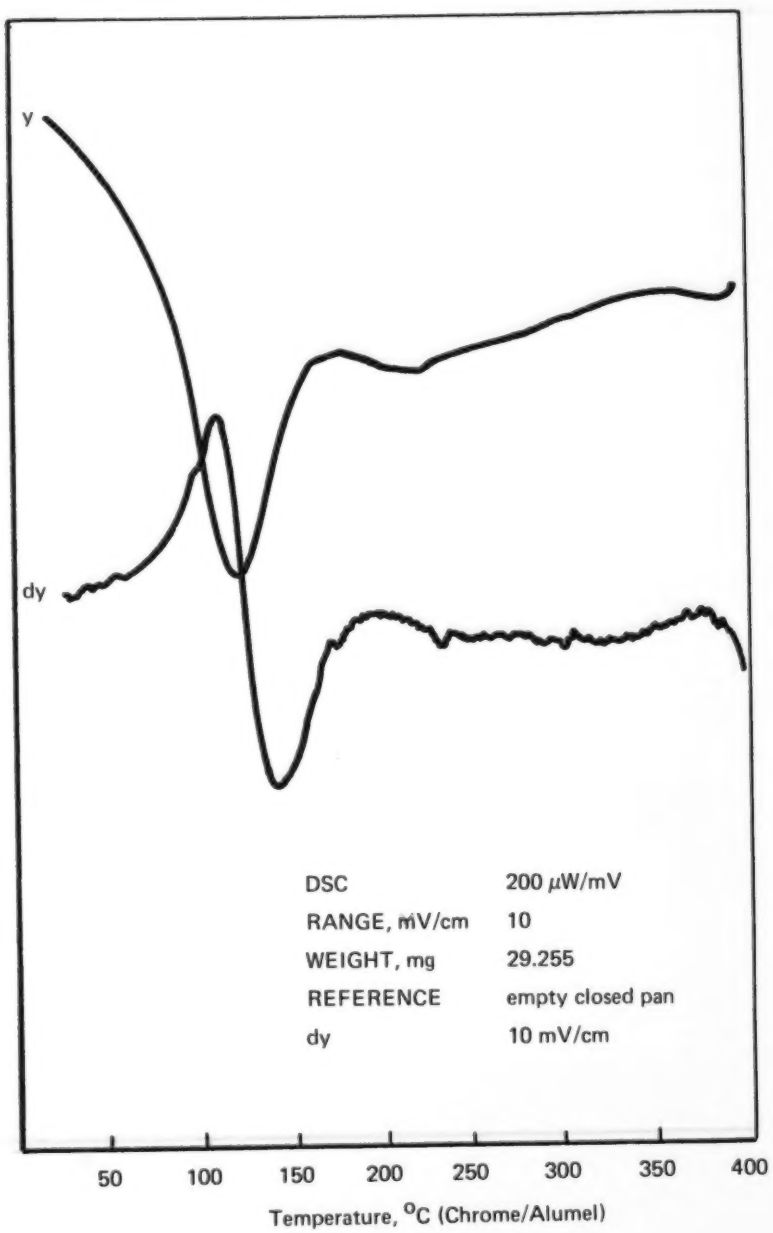

FIGURE 6 DIFFERENTIAL SCANNING CALORIMETER TRACES FOR XE-348 RESIN

V. CONCLUSIONS

The work reported here was designed to address several specific topics which resulted from previous studies. In this experimental investigation, two-to-three compounds each from a number of compound categories were used as models to investigate retention and recovery phenomena in various sorbent:sorbate systems. The conclusions that can be developed on the basis of these data are the following:

A. Uncertainty in V_g Values

Review of cumulative sets of data on V_g^T for the same sorbate:sorbent system indicate that uncertainties in values of V_g^{20}, extrapolated from measurements at two or three elevated temperatures, may be as high as a factor of four or five. This uncertainty should be taken into account when comparing data for different sorbate:sorbent systems and in designing sampling systems with appropriate margins of safety to assure quantitative collection of a given sorbate.

B. Alternative Sorbents

Florisil is comparable to XAD-2 and Tenax-GC in terms of its volumetric capacity for collection of the alkanes, alcohols and chlorinated aromatics tested. Florisil showed very much higher (ca 10^4X) capacity for the chlorinated aliphatic species (dichloroethane, dichloropropane) tested than either XAD-2 or Tenax-GC. It may be the sorbent of choice for collection of volatile chlorinated organics in applications, such as ambient air monitoring, in which large volumes must be sampled to meet detection limit constraints. The low blank values obtainable by thermal activation of Florisil is also an advantage for such applications.

Limited data obtained for aliphatic hydrocarbon sorbates suggest that recovery from Florisil may be less than quantitative. Also, the possible effects of moisture on Florisil V_g's should be investigated to determine its suitability for stack sampling applications.

Ambersorb XE-340,[3] XE-347 and Amberlite XAD-7 have substantially greater capacity for collection of low molecular weight alcohols than do XAD-2 and Tenax-GC. Recovery of alcohols from Ambersorb XE-340 was also found to be satisfactory (75-88%); recovery from charcoal and from XAD-7 was less than 50% in several tests. Ambersorb XE-340/347 are therefore suggested for applications involving sampling specifically for volatile alcohols.

C. Organometallics

The volumetric capacity of XAD-2 was found to be adequate for collection of two organometallic compounds tested--tetraethyllead and diethylmercury. Values of V_g^T for organometallics on XAD-2 are very similar to those of organic species with similar boiling points, measured at the same temperature.

D. Effects of Methane Atmospheres on V_g^T for XAD-2

Data for aliphatic hydrocarbon and alcohol sorbates indicate no effect of 1.1% (11,000 parts per million) of methane on the volumetric capacity of XAD-2.

E. Effects of Mixtures of Sorbates

Data for an aliphatic, an aromatic hydrocarbon and an alcohol show no evidence of competitive effects on V_g^T when several species are present at parts per million concentrations in the same sample.

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